bond. The shortest non-bonded oxygen–oxygen distances other than edges of the octahedra, are 3·13 Å between O_7 pairs (through a center of symmetry) and 3·22 Å between O_9 and O_4.

We find no reasonable alternative to this hydrogen configuration, and the entropy discrepancy is not explained by our work.

The hydrogen bonds tie the sulfate ions and water octahedra together in a three-dimensional network as indicated in Fig. 2. In this figure, the hydrogen configuration is indicated by small circles on the hydrogen bonds. Because of the bond angles the hydrogen atoms are expected to fall slightly off these lines joining oxygen atoms. We do not have a direct determination of the hydrogen positions from the diffraction data.

The two cobalt ions, Co_1 and Co_2, have point symmetries $\bar{1}$ and 2 respectively. The water octahedron about Co_1 is hydrogen bonded exclusively to sulfate ions. The Co_2 water octahedron has ten hydrogen bonds to sulfate ions and four involving water molecules of neighboring Co_2-type octahedra.

The average interatomic distances are as follows:

S–O(SO_4^{--})	1·46 Å
O–O(SO_4^{--})	2·39 Å
Co–O($Co(H_2O)_6^{++}$)	2·11 Å
O–H–O (hydrogen bond)	2·79 Å

Several other substances have the same structure as $CoSO_4.6H_2O$. In addition to the two magnesium compounds, $CoSeO_4.6H_2O$, $ZnSO_4.6H_2O$, and one form of $NiSO_4.6H_2O$ are isomorphous (Groth, 1908). This structure has been recognized in nature as the minerals hexahydrite, $MgSO_4.6H_2O$, and bianchite, $ZnSO_4.6H_2O$ (Palache, Berman & Frondel, 1952).

A more thorough study of the structure of $MgSO_4.6H_2O$ is in progress, and the location and refinement of the hydrogen parameters in that crystal will be the topic of another article shortly.

We thank Dr Rao and Prof. Giauque for their unpublished thermodynamic data and for valuable discussions.

References

Busing, W. R. & Levy, H. A. (1959). Oak Ridge National Laboratory Report 59-4-37.

Goszner (1907). *Ber. deutsch. chem. Ges.* **40**, 2374.

Groth, P. (1908). *Chemische Kristallographie*, v. 2, 426. Leipzig: Engelmann.

Handbook of chemistry and Physics (1957). 39th Ed., 521. Cleveland, Ohio: Chemical Rubber Publishing Co.

Hartree, D. R. & Hartree, W. (1939). *Proc. Roy. Soc.* A, **238**, 229.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

Marignac, Ch. De (1855). *Arch. sc. phys. et nat. Genève*, (1), **14**, 234. Ouevres **1**, 381.

Palache, C., Berman, H. & Frondel, C. (1952). *Dana's System of Mineralogy*. Vol. II, p. 492. New York: Wiley.

Rao, R. V. G. & Giauque, W. F. (1960). Private communication.

Ruben, H. W., Templeton, D. H., Rosenstein, R. D. & Olovsson, I. (1960). *J. Amer. Chem. Soc.* **83**, 820.

Thorpe & Watt (1880). *J. Chem. Soc., London*, **37**, 102.

Tomiie, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.

Watson, R. E. & Freeman, A. J. (1961). *Acta Cryst.* **14**, 27.

Acta Cryst. (1962). **15**, 1224

The Crystal Structure of $Ce_{24}Co_{11}$*

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(*Received* 5 *February* 1962)

The structure of $Ce_{24}Co_{11}$, the most cerium-rich compound in the Ce–Co system, has been determined by single crystal X-ray methods. The compound is hexagonal, space group $P6_3mc$ with $a = 9·587$ and $c = 21·825$ Å, $Z = 2$. The structure was solved by applying Buerger's minimum function. Nearly all of the Ce atoms have rather close Co neighbors, some Ce–Co distances being as short as 2·61 Å.

Introduction

Vogel (1947), in a study of the cerium–cobalt phase diagram, reported Ce_3Co as the most cerium rich compound in the system. Coffinberry (1960) prepared alloys of this composition but was unable to obtain a single phase, excess cerium always being present. In fact, alloys containing as much as 30 at.% cobalt contained a small amount of excess cerium. It was not possible to establish the exact formula of this cerium rich compound by using metallographic techniques although it was known that the composition was approximately 30 at.% cobalt.

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

Experimental

An alloy containing 30 at.% cobalt was arc melted and then heat treated in an evacuated quartz tube for about two months at 400 °C. It was then rapidly cooled to room temperature. The density of the as-cast button, before heat treatment, was found to be 7·59 g.cm.$^{-3}$. A portion of the button was crushed and small single crystals were readily obtained from the fragments. The crystals ordinarily oxidize slowly in air but a coating of Duco cement retarded oxidation for several weeks. Single crystals were initially examined with a precession camera and were found to be hexagonal with Laue symmetry $6/mmm$. Reflections of the type hhl with $l=2n+1$ were systematically absent. Possible space groups therefore are $P\bar{6}2c$, $P6_3mc$ and $P6_3/mmc$. The actual space group is shown by the structure determination to be $P6_3mc$.

Lattice parameters were measured accurately with a carefully aligned single-crystal orienter on an XRD-5 apparatus and were found to be $a=9·587 \pm 0·003$ and $c=21·825 \pm 0·010$ Å (λ Mo $K\alpha_1=0·70926$ Å). Intensities were also measured with the single-crystal orienter, by using Mo $K\alpha$ radiation, within a sphere defined by $2\theta \leq 50°$. Of the 630 non-equivalent reflections in this sphere, 435 were observed.

The crystal was mounted so that the $h00$ reflections occurred at $\chi=90°$. The intensity of these reflections is ideally independent of the angle φ provided that the crystal and instrument are accurately aligned. Any variation in intensity as a function of φ results primarily from appreciable absorption coupled with a non-circular cross-section in the crystal. The experimental variation of intensity with φ can form the basis for an empirical 'φ correction', and if more than one reflection is available at $\chi=90°$, this φ correction can also be made a function of θ.

Buerger (1960) has pointed out that when absorption is large it is better to apply an approximate correction than none at all. The crystal fragment used had an average diameter of 0·073 mm. The linear absorption coefficient is 384 cm.$^{-1}$; hence, a spherical absorption correction appropriate for $\mu R=1·4$ was applied. In addition an empirical φ correction was also applied. This correction was not large and varied from about 0·95 to 1·20. Only 37 reflections had a φ correction greater than 1·10. It should be expected, then, that the results with and without the φ correction should be about the same. With the φ correction the final R was 10·3% and without the φ correction it was 10·8%. It is to be noted that in nearly all cases where the correction was $>1·10$ the agreement was improved. Lorentz and polarization corrections were also applied to give a final set of relative values for $|F_{hkl}|^2$.

Determination of the structure

The exact formula of the compound was uncertain until the structure determination was completed. The compound was known to contain about 30 at.% cobalt and there was metallographic evidence indicating that the amount of cobalt was slightly greater than 30 at.%. All of the three possible space groups require an even number of each kind of atom. Unit cell contents compatible with the measured density of 7·59 g.cm.$^{-3}$ were 2 $Ce_{24}Co_{11}$ and 4 $Ce_{12}Co_5$. The calculated densities for these unit cell contents are respectively 7·67 and 7·55 g.cm.$^{-3}$ and their compositions are 31·4 and 29·4 at.% cobalt. $Ce_{24}Co_{11}$ was considered to be the more likely formula because measured densities tend to be lower than calculated densities.

The composition of the compound is close to that of Ce_7Ni_3, the structure of which has been determined by Roof *et al.* (1961). It was initially thought that these two compounds would be structurally related. Ce_7Ni_3 is hexagonal, space group $P6_3mc$ with $a=9·91$ and $c=6·33$ Å. The a axes of the two cells are about the same but the ratio of the c axes is not a rational number. If the structures were similar they could not be related by a simple variation of stacking sequence. An $h0l$ Patterson projection was initially computed. It showed a striking resemblance to the $h0l$ Patterson projection of Ce_7Ni_3. In retrospect, this resemblance is fortuitous for there is no place in the present structure where a structural unit such as that of Ce_7Ni_3 exists. After the present structure was solved, projections of the two unit cells were graphically superimposed. There is one orientation where some of the Ce atoms project together producing several similar Ce–Ce vectors. There is another orientation where certain Ce atoms project together and where one Ce atom and two Co atoms project near two Ce atoms. Two Ce–Co vectors have about the same weight as one Ce–Ce vector; thus vectors of comparable weight and position are produced in each case. This coincidence was unfortunate for the structure might have been solved more quickly if we had never heard of Ce_7Ni_3.

Study of the $h0l$ Patterson projection did not lead to a solution nor was it possible to establish the space group as $P6_3mc$ by the absence of $0, 0, z$ vectors. A three dimensional Patterson was then calculated. It was still not possible to deduce the structure although much useful information was obtained. It became clear, however, that the space group is $P6_3mc$ and all atoms are on the mirror planes in sets a, b and c of that space group. Also, four sixfold Ce atoms are in set c with $x \approx 0·20$. There are three other sixfold Ce atoms in set c; two with $x \approx \frac{1}{8}$ and one with $x \approx 0·46$ or one at $x \approx \frac{1}{8}$ and two at $x \approx 0·46$. There was no room to place another sixfold Ce atom so the remaining Ce atoms, however many there were, had to be placed in sets a and b. Many arrangements of Ce atoms in these sets and with Co atoms in the remaining holes at $x \approx \frac{1}{8}$ or 0·46 were subjected to least-squares refinement. Large temperature factors for some atoms would invariably result, indicating wrong solutions. R factors as low as 15% occasionally resulted although one or more atoms would be nearly wiped out by a large temperature factor. The correct scheme for stacking the atoms in the indicated positions was not discovered by this technique.

Finally, the solution was found by applying Buerger's (1951) minimum function. If all the atoms were, indeed, lying on the mirror, superpositions of the mirror plane on itself should, in principle, be sufficient to produce the solution. Thus the superpositioning, although performed in three dimensional space was for this case a two dimensional problem. Because of the particular pairs of x coordinates of the various atoms, there were many vectors accidently on or nearly on the mirror plane, which caused difficulty. However, the vector between Ce$_1$ and Ce$_6$ could be interpreted unambiguously. The initial double superposition was made at the Ce$_1$–Ce$_6$ vector and the similar vector related by the screw axis. This first minimum function revealed the stacking arrangement of Ce$_2$, Ce$_3$ and Ce$_4$ at $x \approx 0{\cdot}20$. Superpositions were then made on all of the Ce$_1$–Ce$_2$, Ce$_3$, Ce$_4$, Ce$_6$ vectors and Ce$_5$, Ce$_7$ and Ce$_8$ were revealed. A final superposition on all of the appropriate known Ce$_1$–Ce$_i$ vectors was made, and taking steric factors into account, Co$_1$, Co$_2$ and Co$_3$ were revealed. Successive difference Fouriers then showed the approximate positions of Ce$_9$, Ce$_{10}$, Co$_4$ and Co$_5$.

Systematic application of the minimum function and difference Fouriers finally yielded a model that could be refined normally by least-squares. An IBM-704 computer was used for the least-squares as well as the Fourier and minimum function calculations. The full matrix was used in the least-squares refinement. Form factors were used in functional form with the parameters given by Forsyth & Wells (1959). $P6_3mc$ is a polar space group so the z of Ce$_1$ was fixed arbitrarily at 0·0. The final parameters are listed in Table 1. The observed and calculated structure factors, for which $R = 10{\cdot}3\%$, are available from the authors.

Table 1. *Final least-squares parameters of* Ce$_{24}$Co$_{11}$

Atom	Set	x	z	B
Ce$_1$	c	0·2011 ± 7	0·0	1·8 ± 2 Å^2
Ce$_2$	c	0·2016 ± 8	0·1628 ± 6	2·4 ± 2
Ce$_3$	c	0·2029 ± 6	0·4414 ± 6	1·4 ± 2
Ce$_4$	c	0·2065 ± 8	0·7091 ± 6	2·0 ± 2
Ce$_5$	c	0·4580 ± 6	0·3057 ± 6	1·5 ± 2
Ce$_6$	c	0·4586 ± 5	0·5748 ± 6	1·5 ± 2
Ce$_7$	c	0·1245 ± 6	0·8542 ± 6	1·5 ± 1
Ce$_8$	b	1/3	0·8647 ± 8	1·5 ± 3
Ce$_9$	a	0	0·2070 ± 10	3·0 ± 5
Ce$_{10}$	a	0	0·0526 ± 12	3·2 ± 4
Co$_1$	c	0·1456 ± 19	0·2762 ± 12	2·8 ± 6
Co$_2$	c	0·1503 ± 21	0·5881 ± 15	4·0 ± 7
Co$_3$	c	0·4819 ± 16	0·9290 ± 12	2·2 ± 5
Co$_4$	b	1/3	0·0845 ± 27	2·9 ± 10
Co$_5$	a	0	0·4326 ± 22	2·4 ± 9

A three dimensional Fourier section in the mirror plane was computed with phases determined by the final least-squares cycle. This section is shown in Fig. 1.

Table 2. *Interatomic distances in* Ce$_{24}$Co$_{11}$

The number of equivalent distances is given in parentheses

Ce$_1$–Co$_2$	(2)	3·57 ± 5 Å
–Co$_3$	(2)	2·81 ± 4
–Co$_4$	(1)	2·87 ± 10
–Co$_5$	(1)	3·65 ± 8
–Ce$_1$	(2)	3·80 ± 2
–Ce$_2$	(1)	3·55 ± 2
–Ce$_3$	(2)	3·59 ± 2
–Ce$_6$	(2)	3·44 ± 2
–Ce$_7$	(1)	3·42 ± 2
–Ce$_8$	(1)	3·68 ± 3
–Ce$_{10}$	(1)	3·53 ± 5
Ce$_2$–Co$_1$	(1)	2·64 ± 4 Å
–Co$_2$	(2)	3·43 ± 5
–Co$_4$	(1)	2·78 ± 10
–Ce$_1$	(1)	3·55 ± 2
–Ce$_2$	(2)	3·79 ± 2
–Ce$_4$	(2)	3·54 ± 2
–Ce$_5$	(2)	3·78 ± 2
–Ce$_6$	(2)	3·58 ± 2
–Ce$_9$	(1)	3·48 ± 4
–Ce$_{10}$	(1)	4·12 ± 5
Ce$_3$–Co$_1$	(1)	3·72 ± 4
–Co$_2$	(1)	3·32 ± 5
–Co$_3$	(2)	2·74 ± 4
–Co$_5$	(1)	3·38 ± 9
–Ce$_1$	(2)	3·59 ± 2
–Ce$_3$	(2)	3·75 ± 2
–Ce$_5$	(2)	3·64 ± 2
–Ce$_6$	(2)	3·60 ± 2
–Ce$_7$	(2)	3·50 ± 2
–Ce$_{10}$	(1)	4·15 ± 5
Ce$_4$–Co$_1$	(2)	3·38 ± 4
–Co$_2$	(1)	2·80 ± 5
–Ce$_2$	(2)	3·54 ± 2
–Ce$_4$	(2)	3·65 ± 2
–Ce$_5$	(2)	3·69 ± 2
–Ce$_6$	(2)	3·60 ± 2
–Ce$_7$	(1)	3·44 ± 2
–Ce$_8$	(1)	3·99 ± 3
–Ce$_9$	(1)	3·43 ± 4
Ce$_5$–Co$_1$	(2)	2·82 ± 4
–Co$_3$	(1)	2·87 ± 4
–Ce$_2$	(2)	3·78 ± 2
–Ce$_3$	(2)	3·64 ± 2
–Ce$_4$	(2)	3·69 ± 2
–Ce$_5$	(2)	3·59 ± 2
–Ce$_7$	(2)	3·62 ± 2
–Ce$_8$	(1)	3·70 ± 4
Ce$_6$–Co$_2$	(2)	2·71 ± 5
–Co$_3$	(1)	3·33 ± 4
–Co$_4$	(1)	3·46 ± 10
–Ce$_1$	(2)	3·44 ± 2
–Ce$_2$	(2)	3·58 ± 2
–Ce$_3$	(2)	3·60 ± 2
–Ce$_4$	(2)	3·60 ± 2
–Ce$_6$	(2)	3·60 ± 2
Ce$_7$–Co$_1$	(2)	2·83 ± 4
–Co$_3$	(2)	3·50 ± 4
–Co$_5$	(1)	2·68 ± 9
–Ce$_1$	(1)	3·42 ± 2
–Ce$_3$	(2)	3·50 ± 2
–Ce$_4$	(1)	3·44 ± 2
–Ce$_5$	(2)	3·62 ± 2
–Ce$_7$	(2)	3·58 ± 2
–Ce$_8$	(1)	3·48 ± 3
–Ce$_9$	(1)	3·82 ± 4
Ce$_8$–Co$_3$	(3)	2·84 ± 5
–Ce$_1$	(3)	3·68 ± 3
–Ce$_4$	(3)	3·99 ± 3
–Ce$_5$	(3)	3·70 ± 4
–Ce$_7$	(3)	3·48 ± 3
Ce$_9$–Co$_1$	(3)	2·85 ± 5
–Co$_2$	(3)	3·60 ± 6
–Ce$_2$	(3)	3·48 ± 4
–Ce$_4$	(3)	3·43 ± 4
–Ce$_7$	(3)	3·82 ± 4
–Ce$_{10}$	(1)	3·37 ± 6
Ce$_{10}$–Co$_2$	(3)	2·61 ± 7
–Co$_5$	(1)	2·62 ± 9
–Ce$_1$	(3)	3·53 ± 5
–Ce$_2$	(3)	4·12 ± 5
–Ce$_3$	(3)	4·15 ± 5
–Ce$_9$	(1)	3·37 ± 6
Co$_1$–Ce$_2$	(1)	2·64 ± 4
–Ce$_3$	(1)	3·72 ± 4
–Ce$_4$	(2)	3·38 ± 4
–Ce$_5$	(2)	2·82 ± 4
–Ce$_7$	(2)	2·83 ± 4
–Ce$_9$	(1)	2·85 ± 5
Co$_2$–Ce$_1$	(2)	3·57 ± 5
–Ce$_2$	(2)	3·43 ± 5
–Ce$_3$	(1)	3·32 ± 5
–Ce$_4$	(1)	2·80 ± 5
–Ce$_6$	(2)	2·71 ± 5
–Ce$_9$	(1)	3·60 ± 6
–Ce$_{10}$	(1)	2·61 ± 7
Co$_3$–Ce$_1$	(2)	2·81 ± 4
–Ce$_3$	(2)	2·74 ± 4
–Ce$_5$	(1)	2·87 ± 4
–Ce$_6$	(1)	3·33 ± 4
–Ce$_7$	(2)	3·50 ± 4
–Ce$_8$	(1)	2·84 ± 5
Co$_4$–Ce$_1$	(3)	2·87 ± 10
–Ce$_2$	(3)	2·78 ± 10
–Ce$_6$	(3)	3·46 ± 10
Co$_5$–Ce$_1$	(3)	3·65 ± 9
–Ce$_3$	(3)	3·38 ± 9
–Ce$_7$	(3)	2·68 ± 9
–Ce$_{10}$	(1)	2·62 ± 10

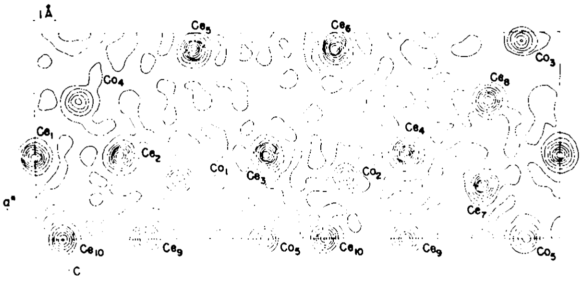

Fig. 1. Electron density in $Ce_{24}Co_{11}$ on the mirror $(x, 2x, z)$ plane. The outer contour is 0 e.Å^{-3}. The contour interval at the Co atoms is 10 e.Å^{-3} and at the Ce atoms 20 e.Å^{-3}.

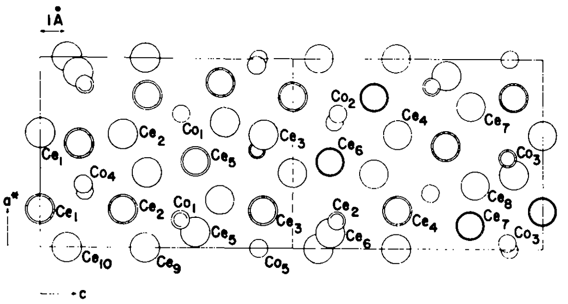

Fig. 2. Projection of the structure of $Ce_{24}Co_{11}$ on a plane normal to the b axis.

Discussion of the structure

A projection of the structure normal to the b axis is shown in Fig. 2. The interatomic distances are listed in Table 2. The neighbors given are those which satisfy the definition of Frank & Kasper (1958). Some of the Ce–Co distances are exceptionally short. The smallest known Ce–Ce distance is 3·09 Å in $CeCo_2$. The radius of Co is about 1·25 Å so one might expect a minimum Ce–Co distance of about 2·80 Å. Distances as short as 2·61 Å are found in this compound. The standard deviations given in Table 2, aside from systematic errors, are overestimates because the fact that the atoms are in special positions has not been taken into account.

We are indebted to V. O. Struebing for the preparation and heat treatment of the alloy.

References

Buerger, M. J. (1951). *Acta Cryst.* **4**, 531.
Buerger, M. J. (1960). *Crystal Structure Analysis*, p. 218. New York: Wiley.
Coffinberry, A. (1960). Private communication.
Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.
Frank, F. C. & Kasper, J. S. (1958). *Acta Cryst.* **11**, 184.
Roof, Jr., R. B., Larson, A. C. & Cromer, D. T. (1961). *Acta Cryst.* **14**, 1084.
Vogel, R. (1947). *Z. Metallk.* **38**, 97.

Acta Cryst. (1962). **15**, 1227

The Crystal Structure of Rhodanine, $C_3H_3ONS_2$*

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(*Received* 5 *May* 1959 *and in revised form* 5 *September* 1961)

The structure of rhodanine has been determined by three-dimensional Fourier and least squares methods using an I.B.M. electronic computer. The crystals are monoclinic having the unit-cell dimensions $a_0 = 10{\cdot}02$, $b_0 = 7{\cdot}67$, $c_0 = 7{\cdot}28$ Å; $\beta = 102^\circ\ 38'$. There are four molecules per unit cell and the space group is $P2_1/n$. The molecule is planar. There are two strong N · · · O hydrogen bonds around the center of symmetry, binding the molecules in pairs.

Introduction

The crystal structure of rhodanine

$$\underbrace{CH_2-S-C(=S)-NH-C(=O)}$$

is one of several investigations being carried out in this laboratory on chelate compounds and organic compounds forming chelates. An earlier communication with the unit cell dimensions has appeared (Merritt & Lessor, 1955). Rhodanine has been long used as an intermediate in the preparation of phenylalanine. The analytical properties were not discovered until Feigl (1926) reported the formation of the water–insoluble complex of rhodanine and silver ion. He also found that similar complexes were formed in acidic solution with univalent mercury and copper ions. In basic solution almost all metallic ions give precipitates containing rhodanine which decompose

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